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16. Abstract

Under conditions applicable to the middle stratosphere, the kinetics of the gas phase reaction between $O(^3P)$ atoms and N_2O_5 have been measured in a discharge-flow mass spectrometer by observing the N_2O_5 fragmentation pattern at various O-atom concentrations as a function of injector distance and reactor temperature. At O-atom concentrations of 5-10 x 10^{14} molecules/ cm^3 and a total pressure of 4 Torr, the decay of N_2O_5 was small and only slightly greater than the data scatter. From the known reaction time, O-atom concentration, and experimental uncertainty, upper limits to the rate of reaction (1), $O + N_2O_5$ = Products, can be calculated at the two temperatures for which measurements were carried out (226° and 300°K): $k_1^{300} \lesssim k_1^{226} \leq 3 \times 10^{-1}$ cm^3/molecule-sec. Interference by NO_2 and HNO_3 impurities was taken into account in the experiments and possible interference by product molecules is discussed. The stated upper limit to the value of k_1 indicates that reaction (1) is unlikely to be important in the chemistry of the stratosphere.

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PREFACE

We wish to express our appreciation to H. Niki for his sound advice during these experiments.

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I. Introduction

The chemistry of the nitrogen oxide species in the stratosphere has been the subject of much research in recent years [1] because of the possibility of anthropogenic perturbations on that chemistry. One chain of reactions leads from the reactive oxides, NO and NO_2, to the less reactive species, N_2O_5 and HNO_3:

$$NO + O_3 = NO_2 + O_2;$$
$$NO_2 + O_3 = NO_3 + O_2;$$
$$NO_2 + NO_3 = N_2O_5;$$

$$N_2O_5 + H_2O \overset{\text{surface}}{=} 2HNO_3 \text{ (?)}.$$

Very little information is available concerning the chemistry of N_2O_5. In his discussion of the catalytic reduction of stratospheric ozone by nitrogen oxides, Johnston [1] discussed, in addition to the above reactions, the photolysis of N_2O_5 and its possible reaction with $O(^3P)$ atoms,

$$O + N_2O_5 = \text{Products}, \qquad (1).$$

On the basis of the data available, Johnston calculated a 9 hr half life for N_2O_5 photolysis at 20 km, with the value decreasing sharply at higher altitudes. Only one study of the reaction of $O(^3P)$ atoms with N_2O_5 has been reported, [2] in which the flash photolysis resonance flourescence technique was used to produce and monitor O atom concentration in the presence of N_2O_5. This method could only produce an upper limit to the rate constant ($k \leq 2 \times 10^{-13}$ cm^3/molecule-sec) because of the unavoidable presence in the N_2O_5 of NO_2, which rapidly consumes $O(^3P)$ atoms. Using this upper limit as the value of k_1, and using a value of the $O(^3P)$ concentration which is typical of the stratosphere at 30 km (10^8 molecules/cm^3), [3] the half life of N_2O_5 would be $\sim$9 hrs. Thus, this reaction could be important in the NO_x chemistry of the stratosphere. In the present investigation, reaction (1) was studied as a function of temperature by the discharge flow method. A quadrupole mass spectrometer was used to directly measure the N_2O_5 concentration, eliminating the problem of NO_2 interference encountered when the oxygen atom concentration is monitored.

II. Experimental

All experiments were carried out in a jacketed Pyrex flow tube, 85 cm long and 1.5 cm i.d. (Figure 1). All surfaces in the flow tube were coated with a saturated solution of aqueous H_3BO_3 to reduce atom recombination. Oxygen atoms, $O(^3P)$, were formed in a side arm by the rapid titration reaction of NO (UHP*) with $N(^4S)$ atoms generated by a 2450 MHz microwave discharge in a stream of N_2 (UHP*). The $O(^3P)$ concentration (5-10 x 10^{14} molecules/cm^3) was maintained 5-30 times greater than the N_2O_5 concentration throughout the experiments. The $O(^3P)$ concentration was measured at several positions along the length of the tube by NO_2 titration at room temperature. [4] During the low temperature experiments (223 ± 10°K), a modification of this titration was used because the titration reaction seemed to slow down in our flow tube. This slow down in rate has been observed previously. [5] At the low temperatures, we overtitrated the $O(^3P)$ with a 3 - 5 fold excess of NO_2 to drive the reaction to completion and observed the NO_2 signal at 46 amu. The O atom concentration could be determined from the total NO_2 flow rate and the observed consumption of the NO_2, measured at 46 amu, when the microwave discharge was turned on.

The N_2O_5 was introduced into the flow reactor in a stream of Ar (UHP*) via a multiple hole sliding injector. The total reactor pressure (~95% N_2) was 4.5 Torr as measured at the injector tip, giving a linear flow velocity of 260 cm/sec at room temperature. Flow rates of all gases were measured by volume flow meters which were calibrated as mass flow meters by monitoring the pressure rise in calibrated volumes as a function of time. These calibrations were rechecked periodically during the investigation.

The contents of the flow tube were sampled through a 0.05 cm diameter nozzle orifice which penetrated approximately 1 cm into the end of the flow tube. The resultant molecular beam was modulated by a tuning fork chopper operated at 400 Hz and then entered an electron impact ionizer which was coupled to a quadrupole mass analyzer. Both $O(^3P)$ and N_2O_5 were monitored, the latter at mass 46 because it did not exhibit a parent ion peak or any ion peak greater than 46 amu. The fragmentation pattern of N_2O_5 at 27 eV electron bombardment energy was characterized by the ratio of ion intensities,

*Ultrahigh Purity

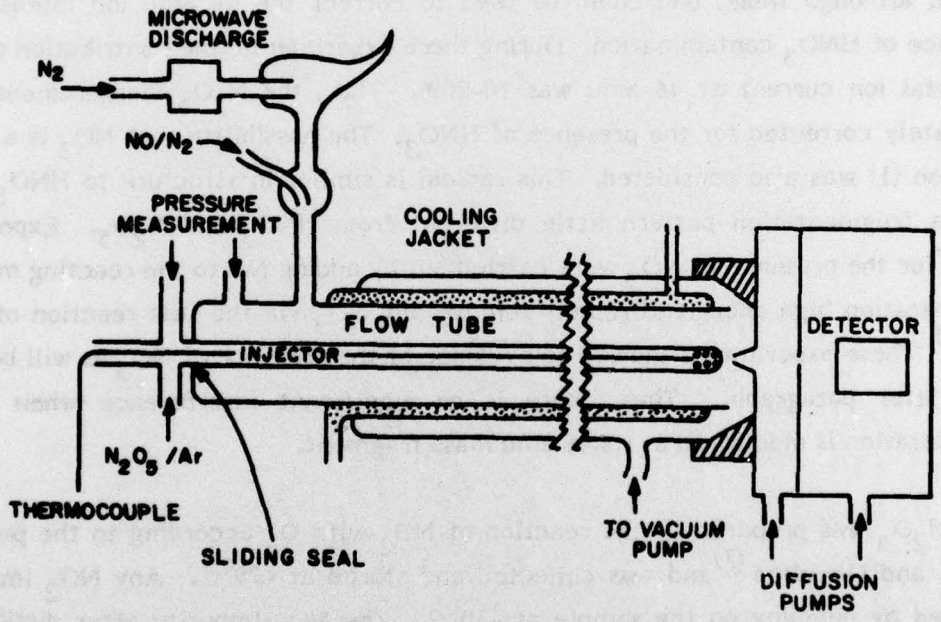

Figure 1. SCHEMATIC OF THE EXPERIMENTAL APPARATUS.

I(46 amu)/I(30 amu) = 8. Because no parent ion peak was visible, possible interferences at 46 amu from other molecules had to be considered. No interference from NO_2 occurred since the measurements were made in the presence of a large excess of $O(^3P)$, which will react rapidly with any NO_2 present, either as a contaminant in the N_2O_5 or formed from reaction (1), and yield NO + O_2. If N_2O_4 were a product of reaction (1), the N_2O_4 would dissociate with a half life of $\sim$ 1m sec under our experimental conditions, and the NO_2 formed would again be converted rapidly to NO. Thus, neither NO_2 nor N_2O_4 will interfere with N_2O_5 measurement at 46 amu in the presence of a substantial concentration of $O(^3P)$ atoms. HNO_3 has a fragmentation pattern nearly identical to that of N_2O_5 and does not react with O atoms at an appreciable rate. [6] Thus, HNO_3 could produce interference at 46 amu. However, the parent peak of HNO_3 at 63 amu was visible, although weak, and could be used to correct the 46 amu ion intensity for the presence of HNO_3 contamination. During these experiments, the contribution of HNO_3 to the total ion current at 46 amu was 10-20%. Thus, the N_2O_5 measurements could be accurately corrected for the presence of HNO_3. The possibility that NO_3 is a product of reaction (1) was also considered. This radical is similar in structure to HNO_3 and could have a fragmentation pattern little different from HNO_3 and N_2O_5. Experiments to check for the presence of NO_3 were carried out by adding NO to the reacting mixture at a concentration high enough to rapidly remove any NO_3 via the fast reaction of NO_3 with NO. [3] These experiments showed no evidence of the presence of NO_3 as will be discussed in a later paragraph. Thus, there is no significant interference when the N_2O_5 concentration is monitored at its 46 amu mass fragment.

N_2O_5 was prepared by the reaction of NO_2 with O_3 according to the procedure of Schott and Davidson [7] and was collected and stored at -79°C. Any NO_2 impurity was removed by pumping on the sample at -10°C. The NO_2 impurity after distillation was estimated to be < 5% by observing the decrease in the 46 amu mass peak after a short reaction time in the presence of $O(^3P)$ atoms. The presence of HNO_3, presumably formed by the hydrolysis of N_2O_5, was also observed as a minor impurity as stated above. The N_2O_5 concentration in the flow tube during the experiments ranged from 3×10^{13} to 1.5×10^{14} molecules/cm^3 as estimated by its conversion to NO in an electric discharge.

During the low temperature experiments, the flow tube temperature was controlled by circulating chilled methanol through the flow tube jacket. Temperatures were

regulated to $\pm 2^{\circ}C$ and were monitored during the experiments by a thermocouple inserted into the injector tube. The thermocouple, except for the sensing tip, was enclosed in a Teflon sleeve to minimize possible surface catalyzed decomposition of the N_2O_5 during injection.

In order to check the calibration of our flow tube, we also made preliminary measurements of the rate constants of the reactions of $O(^3P)$ atoms with C_2H_4 and C_4H_{10}. The rate constants obtained for these reactions were $7.0(\pm 3.0) \times 10^{-13}$ cm^3/molecule-sec and $1.0\ (\pm 0.5) \times 10^{-14}$ cm^3/molecule-sec respectively. While the latter value might be somewhat low, both values are in reasonable agreement with previously published values.[8,9]

III. Results

Figure 2 presents the results from a series of three room temperature experiments. In the figure, the ratio of the N_2O_5 concentration in the presence and absence of $O(^3P)$ atoms, $[N_2O_5]/[N_2O_5]_o$, is plotted as a function of distance of the injector from the detector nozzle. The ion signals at 46 amu have been corrected for the presence of the measured HNO_3 impurity as described previously. The $O(^3P)$ concentrations in the reactor at a linear flow velocity of 260 cm/sec were 9.3, 6.9, and 6.5×10^{14} molecules/cm^3 for the three measurements with a gradient of 25% down the length of the tube resulting from atom recombination.

For each set of data, there is a 2-5% drop in the 46 amu ion intensity in the presence of $O(^3P)$ atoms at the shortest measured reaction times. This is identical in magnitude to the decrease observed in the presence of $N(^4S)$ atoms, suggesting that this decrease arose from the reaction of $O(^3P)$ or $N(^4S)$ with a small amount of NO_2 present as a contaminant in the N_2O_5 sample. Since these reactions are sufficiently fast that they proceed to completion even at the shortest reaction times measured,[3] the reaction rate of $O(^3P)$ with N_2O_5 at $300^{\circ}K$ can be determined from the slopes of the curves in Figure 2 with no correction.

The data show that only a very small decrease occurs in the N_2O_5 concentration as the injector distance from the sampling nozzle is increased. The magnitude of the decrease is only slightly greater than the data scatter and can not be used to estimate a

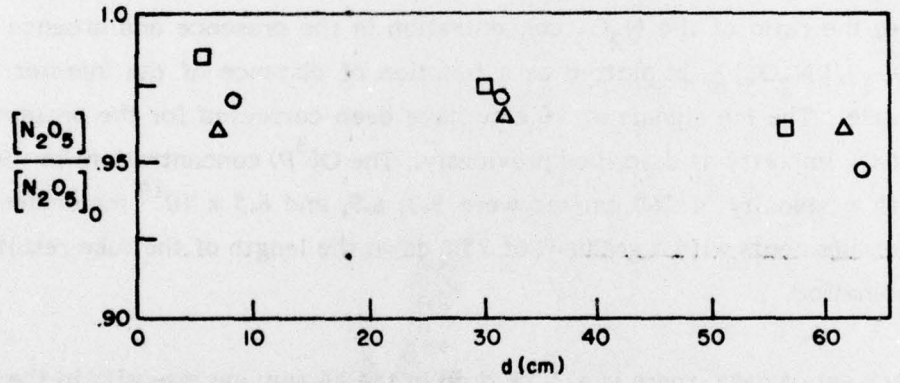

Figure 2. DECAY OF N_2O_5 IN THE PRESENCE OF $O(^3P)$ ATOMS AS A FUNCTION OF THE DISTANCE OF THE INJECTOR FROM THE END OF THE FLOW REACTOR AT 300° K. $[N_2O_5] / [N_2O_5]_0$ represents the ratio of the ion intensity at 46 amu in the presence of O atoms to the intensity in the absence of O atoms. Each data point represents the average of at least 4 separate measurements. Each set of three data points was obtained during one day's measurements at $O(^3P)$ concentrations of 9.3×10^{14} (□), 6.9×10^{14} (Δ), and 6.5×10^{14} (O) molecules/cm^3. In all measurements, the linear flow velocity was 260 cm/sec at a total pressure of 4.5 Torr.

valid rate constant particularly since the possibility of a slow unknown interfering reaction does exist. However, the data can be used to evaluate an upper limit to k_1 by drawing the best straight lines through each individual set of data and obtaining the value of k_1 under the conditions stated in the figure. The average value of the three data sets obtained using this method, including estimates of both systematic and random errors, is $k_1 \leq 1.0(^{+2.0}_{-0.7}) \times 10^{-16}$ cm^3/molecule-sec.

Figure 3 presents similar data for reaction (1) at three lower temperatures characteristic of the stratosphere, 233°, 224°, and 213°K. The O(^{3}P) concentrations for the three runs were 10.0, 6.1, and 4.0 x 10^{14} molecules/cm^3 at a linear flow velocity of 200 cm/sec. The results were similar to those obtained at 300°K. Calculated in the manner described, the upper limit to k_1 at 223 ± 10°K is $k_1 \leq 1.5(^{+2.0}_{-0.7}) \times 10^{-16}$ cm^3/molecule-sec.

As mentioned previously, the possibility of interference at 46 amu by NO_3 must be considered. In order to determine the extent of any NO_3 interference, we added an excess (1-2 x 10^{14} molecules/cm^3) of NO during the N + NO titration reaction. The reaction of NO with NO_3,

$$NO + NO_3 = 2NO_2,$$

is very fast ($k = 8.5 \times 10^{-12}$ cm^3/molecule-sec), and any NO_3 generated in reaction (1) would be quickly converted first to NO_2 and thence to NO via reaction with excess O(^{3}P) atoms. This overtitration with NO also catalyzes the recombination of O(^{3}P) atoms via the series of reactions:

$$NO + O \overset{M}{=} NO_2,$$
$$NO_2 + O = NO + O_2.$$

At the stated excess NO concentration, the O(^{3}P) recombination produced a gradient of approximately a factor of 3-6 in the O(^{3}P) concentration along the length of the flow tube. Experiments performed at 220° and 300°K showed that the presence of excess NO did not change the ion intensity at 46 amu within experimental error. The upper limit to k_1 calculated from these experiments was $k_1 \leq 5 \times 10^{-16}$ cm^3/molecule-sec. This value

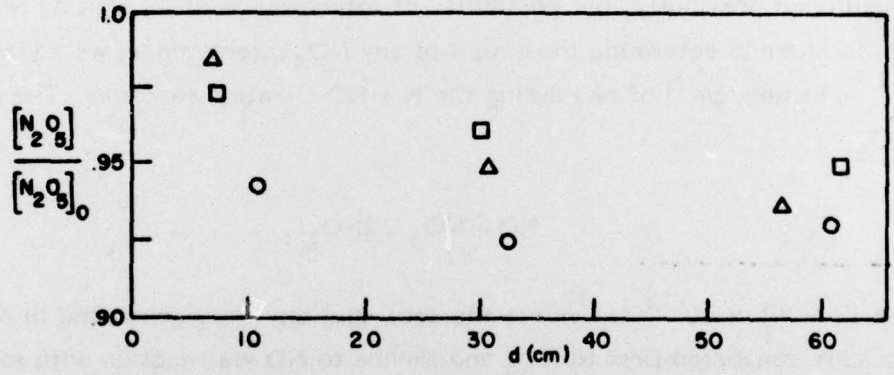

Figure 3. DECAY OF N_2O_5 IN THE PRESENCE OF $O(^3P)$ ATOMS AS A FUNCTION OF THE DISTANCE OF THE INJECTOR FROM THE END OF THE FLOW REACTOR AT 223 ± 10^0 K. $[N_2O_5] / [N_2O_5]_0$ represents the ratio of the ion intensity at 46 amu in the presence of O atoms to the intensity in the absence of O atoms. Each data point represents the average of at least 4 separate measurements. Each set of three data points was obtained during one day's measurements at $O(^3P)$ concentrations of 1×10^{15} (Δ), 6.1×10^{14} (□), and 4.1×10^{14} (O) molecules/cm^3. In all measurements, the linear flow velocity was 200 cm/sec at a total pressure of 4.5 Torr.

was obtained using a computer model which included the gradient in the $O(^3P)$ atom concentration along the length of the reactor. The upper limit is somewhat higher because of the decreased O atom concentration, but the results demonstrate that no measurable interference at 46 amu from NO_3 radicals was present in these experiments.

IV. Discussion

The data presented in Figures 2 and 3 indicate that in our experimental apparatus there is no clear evidence of a reaction between $O(^3P)$ atoms and N_2O_5 in the temperature range 223^o-300^oK. The upper limit to the bimolecular rate constant for the reaction at both temperatures is $k_1 \leq 3 \times 10^{-16}$ cm^3/molecule-sec, using the maximum of the previously stated error limits. This upper limit is three orders of magnitude slower than that reported previously. [2]

In terms of the stratospheric chemistry of N_2O_5, the upper limits derived in our experiments for its reaction with $O(^3P)$ atoms indicate a half-life of approximately 1 year at 30 km as a result of this reaction. Since the photolysis of N_2O_5 is three orders of magnitude faster, the reaction of $O(^3P)$ atoms with N_2O_5 is unlikely to be significant in the chemistry of the stratosphere.

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